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High-energy X-ray diffraction studies of i-Sc12Zn88

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Abstract

Although quasicrystals form in a wide variety of ternary and quaternary metallic alloys, examples of stable binary icosahedral quasicrystals are quite rare. Indeed, it has been a decade since the discovery of icosahedral phases in Yb–Cd and Ca–Cd. We have discovered millimeter-sized facetted grains of i-Sc12Zn88 with icosahedral (pentagonal dodecahedral and rhombic triacontahedral) morphologies in solution-grown samples. Structural characterization of the bulk icosahedral phase was accomplished through single-grain high-energy X-ray diffraction. For both growth morphologies, all diffraction peaks could be indexed by a primitive (P-type) icosahedral phase. The two types of morphology do, however, present interesting differences in their respective degrees of quasicrystalline order.

Keywords

icosahedral, quasicrystal, solution growth, high-energy diffraction

Disciplines

Condensed Matter Physics | Materials Science and Engineering

Comments

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High-energy X-ray diffraction studies of i-$Sc_{12}Zn_{88}$

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Although quasicrystals form in a wide variety of ternary and quaternary metallic alloys, examples of stable binary icosahedral quasicrystals are quite rare. Indeed, it has been a decade since the discovery of icosahedral phases in Yb–Cd and Ca–Cd. We have discovered millimeter-sized facetted grains of i-$Sc_{12}Zn_{88}$ with icosahedral (pentagonal dodecahedral and rhombic triacontahedral) morphologies in solution-grown samples. Structural characterization of the bulk icosahedral phase was accomplished through single-grain high-energy X-ray diffraction. For both growth morphologies, all diffraction peaks could be indexed by a primitive (P-type) icosahedral phase. The two types of morphology do, however, present interesting differences in their respective degrees of quasicrystalline order.

Keywords: icosahedral; quasicrystal; solution growth; high-energy diffraction

1. Introduction

Tremendous progress has been made in our understanding of the structure and physical properties of quasicrystals, but a great deal remains to be uncovered, particularly concerning the formation, stability and growth of these fascinating materials. For example, icosahedral quasicrystals form in a wide variety of ternary and quaternary metallic alloys, but only rarely as stable phases in binary alloys. The discovery [1,2] of stable binary icosahedral phases in Yb–Cd and Ca–Cd alloys a decade ago generated tremendous excitement and opened new opportunities in quasicrystal research. The principle advantages offered by these alloys include: (1) the simplicity of a binary alloy (relative to ternary and higher compositions) for structure determination [3], (2) the fact that the icosahedral phases are very close in composition to the 1/1 crystalline approximants [4], and (3) i-Yb–Cd presents an unusually high degree of structural order for a primitive (P-type) icosahedral structure [5]. Soon after the discovery of i-$YbCd_{5.7}$, an icosahedral phase was identified in Zn–Mg–Sc [6] and a large number of ternary compositions of the type Zn–M–Sc (M=Mn, Fe, Co, Ni, Cu, Pd, Pt, Au, Ag) [7–9]. However, the binary parent phase of this series had not yet been synthesized.

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2. Growth and characterization of i-$Sc_{12}Zn_{88}$

Recently, we reported on the discovery of a stable binary icosahedral phase with a composition of $Sc_{12}Zn_{88}$ [10]. Single grains of i-$Sc_{12}Zn_{88}$ quasicrystals were produced using solution-growth methods [11,12]. For all growths, high-purity Sc and Zn were placed in a crucible, and sealed in a silica tube back filled with approximately 0.25 atmosphere of high-purity Ar. Starting compositions, ranging from Sc_4Zn_{96} to Sc_2Zn_{98}, were heated to 950°C, cooled to 800°C over several hours, and then slowly cooled to 480°C over 30–70 h. At this temperature, the growths were removed from the furnace and the remaining liquid decanted. Upon opening the crucibles, facetted grains, as large as 1 mm in size, in the shape of either a pentagonal dodecahedron (PD) or rhombic triacontahedron (RT) were found either on the surfaces of crystals of the cubic $ScZn_6$ phase, on the strainer surface, or on the walls of the crucible itself (Figure 1).

Powder diffraction measurements on crushed samples of both the PD and RT grains were done to characterize the icosahedral structure and check for the presence of second phases [10]. All diffraction peaks could be indexed by a primitive (P-type) icosahedral structure with $a_R = 5.017(3)$ Å or a 6D lattice constant of 7.095(4) Å, close to the values obtained for the ternary Zn–M–Sc icosahedral alloys.

Wavelength dispersive X-ray spectroscopy was used to establish the stoichiometry of the PD and RT grains and to rule out the possibility of a third element impurity, leading to a ternary phase. The composition of both the PD and RT grains was found to be a binary with $12 \pm 0.3\%$ Sc, and no detectable third elements [10]. Differential thermal analysis was employed to determine the decomposition temperature of this new phase (505°C) by heating samples of isolated pentagonal grain [10]. We have also annealed as-grown samples at 390°C for 22 h in one atmosphere of Ar and found neither morphological nor structural changes as evidenced by visual inspection, the X-ray Laue pattern or X-ray powder diffraction.

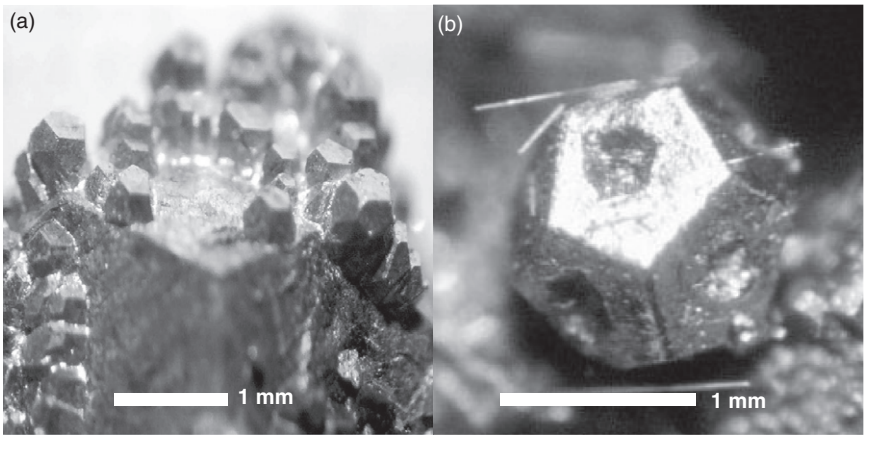

Figure 1. (a) Array of pentagonal dodecahedra on the surface of a large single crystal of the $ScZn_6$ approximant phase. (b) A 1 mm single grain of i-$Sc_{12}Zn_{88}$ exhibiting pentagonal dodecahedral morphology.

3. High-energy X-ray diffraction studies of the perfection of i-$Sc_{12}Zn_{88}$

To further characterize the structures of the PD and RT single grains, high-energy X-ray diffraction measurements were performed on station 6ID-D in the MUCAT Sector at the Advanced Photon Source with the incident beam along the five- and two-fold axes (Figure 2). These data were taken using an incident X-ray energy of 129 keV and recorded on a MAR 345 area detector. The use of high-energy X-rays ensures that the structure of the sample bulk, rather than surface, is probed and, by rocking the sample through small angular ranges about axes perpendicular to the beam, provides an image of reciprocal space planes that lie normal to the beam

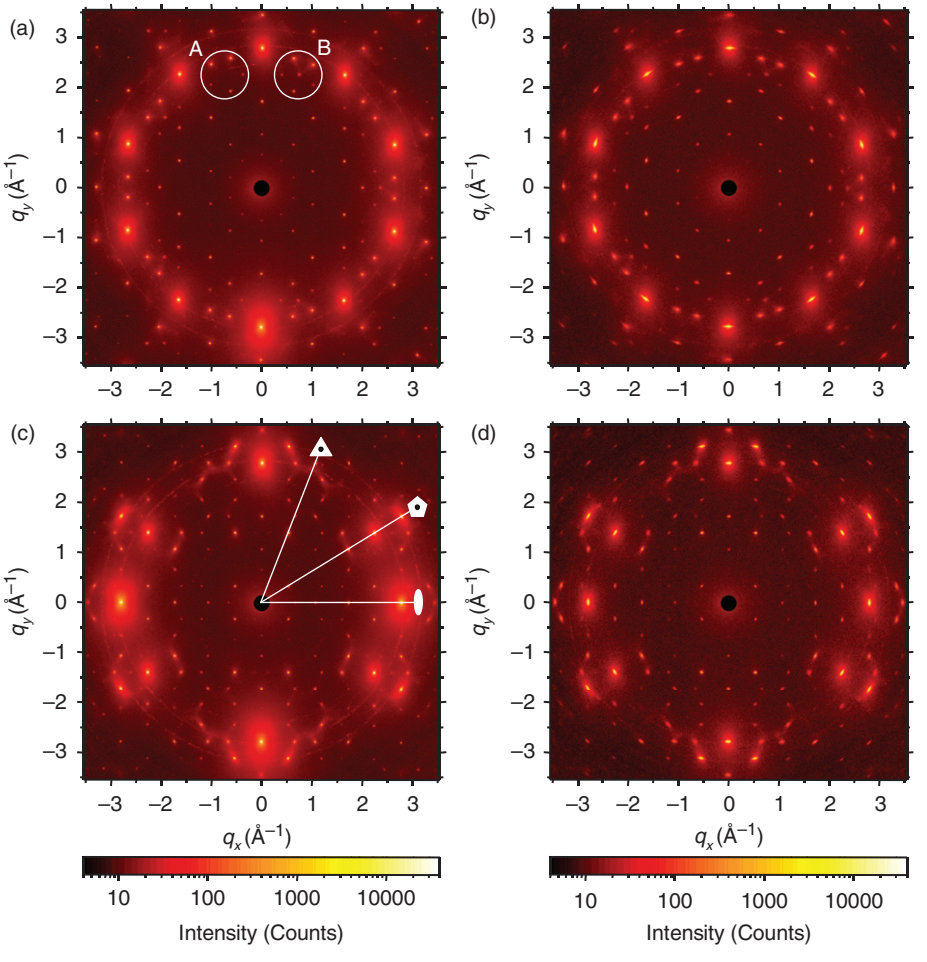

Figure 2. Single-grain high-energy X-ray diffraction patterns measured along the five- and two-fold axes are shown in panels (a) and (c) for the PD grain, and (b) and (d) for the RT sample. The lines in panel (c) indicate the two-, three- and five-fold directions in the two-fold scattering plane. The weak peak in the center of pentagon B in panel (a) is not observed in neighboring pentagon A since it does not originate in the five-fold plane, but slightly above it (within the range over which the sample is rocked).

direction [13]. All diffraction spots in the two- and five-fold planes can be indexed to the icosahedral phase and lie, within the resolution of the detector, at the predicted positions. Note that as one moves from the center to the periphery of the pattern, diffraction spots from higher-order zones are also in evidence. For instance, the weak peak in the center of pentagon B in Figure 2a is not observed in neighboring pentagon A since it does not originate in the five-fold plane but slightly above it (within the range over which the sample is rocked).

Although the diffraction patterns from both the PD and RT grains are consistent with the icosahedral structure, there are some intriguing differences between them. In particular, the diffraction peaks from the PD grain are sharper in both the longitudinal (radial) and transverse directions. The transverse broadening inherent to the RT samples is illustrated in Figure 3, which shows an expanded view of the 28/44 diffraction peak in the five-fold plane of a PD grain (Figure 3a) and an RT grain (Figure 3b). All RT grains investigated in our study show a similar transverse broadening, which indicates some disorder or distortion in the relative orientation of different regions of the sample.

To analyze the systematic behavior of the longitudinal widths of diffraction peaks from the PD and RT grains, the diffraction patterns in Figure 2 were azimuthally integrated to obtain 1D plots of the intensity as a function of radial position in the five- and two-fold planes. We also performed 2D fits of selected sets of individual reflections for the PD sample, with both small and large values of phason momentum, Q_{perp}, to determine whether the widths measured from this azimuthal integration arise from the broadening of diffraction peaks or shifts in their positions relative to the center of the pattern. The centroids of the 2D fits fell within $\pm 0.004\,\text{Å}^{-1}$ of the calculated values indicating the absence of anisotropic phason strain [14] over the bulk of the PD sample. A similar analysis for the RT sample is currently in progress.

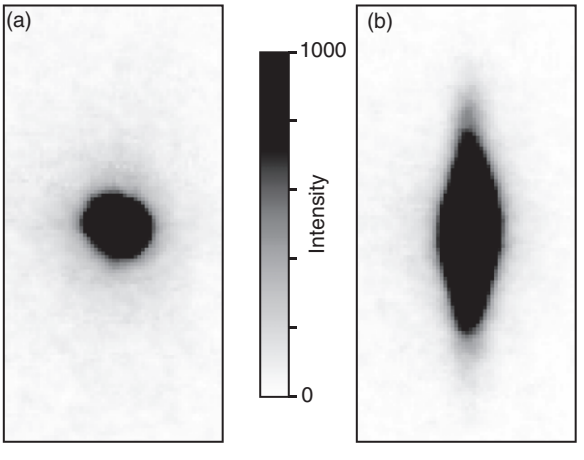

Figure 3. Expanded view of the 28/44 diffraction peak in the five-fold plane from (a) the PD sample and (b) the RT sample, illustrating the difference in transverse broadening for the two morphologies.

Figure 4 shows the longitudinal peak width dependence on both Q (Figure 4a) and Q_{perp} (Figure 4b) for both the PD (open squares: blue online) and RT (circles: red online) samples. For the experimental configuration employed here, the Q-resolution was 0.01 Å^{-1}, determined from measurements on Si powder and single crystals of the $ScZn_6$ approximant phase. As Figure 4 illustrates, there is no clear dependence of peak widths on Q in evidence, whereas we find a distinct linear dependence of the longitudinal widths on Q_{perp}, consistent with previous studies of the diffraction from P-type icosahedral alloys. For reference, the dashed line in Figure 4b describes the systematic peak broadening found previously for i-Al–Li–Cu [14,15]. Taken together with the absence of significant peak shifts or distortion, our data indicate that the peak broadening for the PD grains arises primarily from random linear phason strain. Furthermore, as shown in Figure 4b, we find that the RT grains manifest a larger degree of phason strain than the PD grains, as evidenced by significantly broader longitudinal widths of the peaks and stronger increase of these widths with Q_{perp}. Overall, then, the PD grains are characterized by a higher degree of quasicrystalline order than found for the RT samples.

It is also useful to compare the peak widths obtained in the present study on the binary i-$Sc_{12}Zn_{88}$ with previous measurements on ternary Zn–M–Sc icosahedral alloys. To this end, in Figure 5, we plot the data for the PD sample along with the peak widths obtained from powder diffraction measurements on $Zn_{77}Fe_7Sc_{16}$ by Al-Qadi et al. [16]. Although these data do not show a clear systematic dependence on Q_{perp} over the range of their measurement, the peak widths for $Q_{perp} \leq 1$ Å are comparable to the present study.

4. Further work

The difference in the degree of order between the PD and RT grains, described above, is striking and suggests an intimate connection between formation, growth

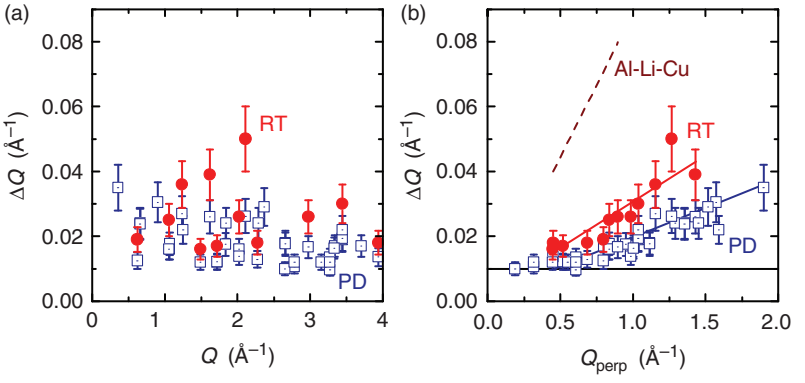

Figure 4. Dependence of the full-width-at-half-maximum (FWHM) of diffraction peaks measured in the two- and five-fold planes of the PD (open squares: blue online) and RT (circles: red online) samples as a function of (a) Q and (b) Q_{perp}. The dashed line represents the trend observed for single grains of i-Al–Li–Cu from [14,15]. The solid black line represents the instrumental resolution limit.

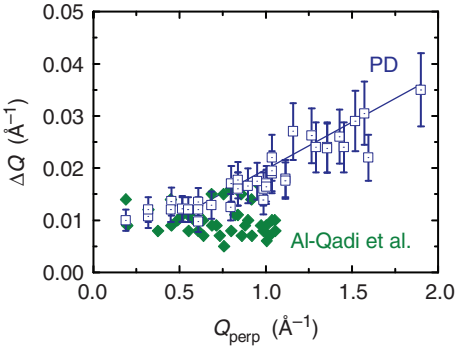

Figure 5. Q_{perp} dependence of peak widths from the present study of the PD single-grain i-$Sc_{12}Zn_{88}$ (open squares: blue online) and the powder diffraction measurements of Al-Qadi et al. (diamonds: green online) [16].

and quasicrystalline order that requires further investigation. For example, the conditions that favor the growth of the PD morphology and corresponding higher degree of quasicrystalline order have not yet been established. It is also not yet clear whether the morphology transforms from one to the other during the growth process itself and, if so, how that is accomplished. The availability of the binary i-$Sc_{12}Zn_{88}$ alloy will allow a more detailed analysis of the role of the M substitutions in Zn–M–Sc alloys including their role in phase formation and stability. Finally, we note that solution growth offers yet another path to the discovery of new quasicrystals and has also led to the production of large, high quality samples of alloys such as icosahedral Al–Pd–Mn, R–Mg–Zn and decagonal Al–Co–Ni [17–19]. The discovery of a stable binary icosahedral alloy in $Sc_{12}Zn_{88}$ suggests that solution growth experiments sampling the cascading peritectics associated with binary liquidus lines may lead to as yet undiscovered binary quasicrystalline alloys.

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